

Note

Synthesis of coupling dinuclear iron complexes from μ -*N*-(2-oxo-2-methylethanaminato)- μ -*N'*-(dimethylamino)- $\text{Fe}_2(\text{CO})_5$ complex with acetylene derivatives

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Abstract

The reactivity of μ -*N*-(2-oxo-2-methylethanaminato)- μ -*N'*-(dimethylamino)- $\text{Fe}_2(\text{CO})_5$ Fe(0) complex with acetylenic derivatives is described. This reaction gives cyclic coupling dinuclear iron carbonyl complexes which were characterized by ¹H, ¹³C, HMQC and HMBC NMR techniques. © 2000 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The reaction between metallic carbonyl complexes with alkynes produces a wide variety of stable organometallic carbonyl complexes and cyclic organic products [1]. Their reactivity, i.e. iron and cobalt complexes, have been demonstrated and applied in organic synthesis. Recently, Pearson [2] reported the reaction of metallic carbonyls

with acetylenic groups as promoter of coupling reactions.

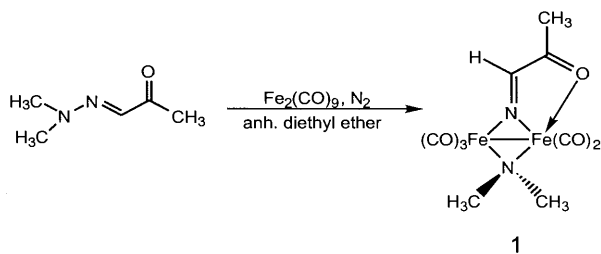
On the other hand, a previous work from our laboratory group reported the formation of μ -*N*-(2-oxo-2-methylethanaminato)- μ -*N'*-(dimethylamino)- $\text{Fe}_2(\text{CO})_5$ complex (**1**) obtained in 50% of global yield [3], from the reaction of $\text{Fe}(\text{CO})_5$ and the monodimethylhydrazone of pyruvaldehyde (Scheme 1).

In this paper we wish to describe the reactivity of complex **1** with some acetylene derivatives, to form heterocyclic dinuclear iron carbonyl complexes (Scheme 2).

2. Results and discussion

The reaction of **1** with acetylenic derivatives gives cyclic coupling products. Some of these reactions present high stereoselectivity due to steric factors, principally.

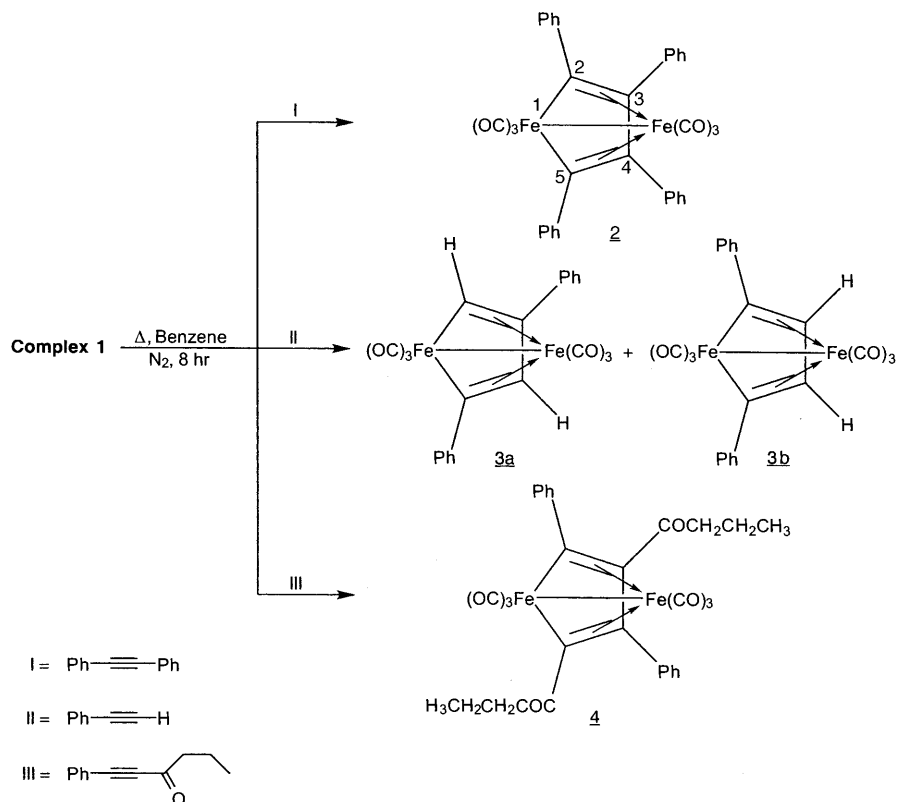
The reaction of **1** and diphenylacetylene affords only one product (**2**, 30%). The structure of the obtained complex was clearly established by a crystallographic study and by a correlation of its spectral and physical



Scheme 1. Synthesis of complex **1**.

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Scheme 2.

Table 1
NMR selected data for **3a**, **3b** and **4**

Complex	¹ H-NMR	¹³ C-NMR	HMQC coupling	HMBC coupling
3a	7.02 (d, <i>J</i> = 3 Hz, 1H, H ₄), (d, <i>J</i> = 3 Hz, 1H, H ₂)	176.79 (C ₃), 149.45 (C ₅), 146.97 (C ₄), 111.25 (C ₂)	146.97 ↔ 7.02 (C ₄ -H ₄), 111.25 ↔ 6.69 (C ₂ -H ₂)	146.97 ↔ 6.69 (C ₄ -H ₂), 111.25 ↔ 7.02 (C ₂ -H ₄)
3b	6.34 (s, 2H)	175.74 (C ₃ , C ₄), 112.08 (C ₂ , C ₅)	175.74 ↔ 6.34	112.08 ↔ 6.34
4	2.44–2.05 (m, 4H), 1.34–1.15 (m, 4H), 0.74 (t, 3H), 0.48 (t, 3H)	204.54 (CO org.), 202.12 (CO org.), 175.47 (C ₃), 170.96 (C ₄), 146.54 (C ₅), 132.90 (C ₂), 46, 44 (αCH ₂), 17, 16 (βCH ₂)		

data with the complex reported by Scharauzer [4], obtained from the reaction of diphenylacetylene and iron pentacarbonyl in 42% reported yield. Nevertheless, in our case this complex is obtained in more gentle experimental conditions.

For the reaction of **1** with phenylacetylene two reaction products were isolated, purified and characterized. For this reaction, there are three possible isomers: the first one has the phenyl groups in 2 and 5 positions of the ferracyclopentadiene moiety. The second possible isomer has the phenyl groups in 3 and 4 positions of the heterocyclic system; the other isomer presents these groups in 2 and 4 positions.

The total identification of the obtained complexes

was made by their spectral data. In the IR spectra the inorganic CO band in each product is observed, and in mass spectrometry the molecular weight of each reaction product was confirmed by high-resolution experiments. Nevertheless, more important data to establish the proposed structures were obtained with the use of ¹H- and ¹³C-NMR, and with HMQC and HMBC experiments (Table 1).

For the first purified complex in ¹H-NMR the following signals are observed: 7.64–7.17 ppm which integrates for ten aromatic hydrogens; 7.02 and 6.69 ppm, two doublet signals with *J* = 3 Hz for each one.

The HMQC spectrum for this complex shows interactions between the signal at 146.97 ppm and the signal

at 7.02 ppm (C_2 -H bond) and another interaction between the signal at 111.25 ppm and the signal at 6.69 ppm (C_4 -H bond).

In the HMBC spectrum we observe the interaction of the signal at 146.97 ppm with the signal at 6.69 ppm and another coupling at three bonds for the signals at 111.25 and 7.02 ppm.

For the possible mentioned structures, all presented data are in agreement only with the structure presented as **3a**.

The second complex obtained and purified shows 1H -NMR signals at 7.32–7.13 ppm which integrate for ten aromatic hydrogens, and a single signal at 6.34 ppm which integrates for two hydrogens. The ^{13}C -NMR spectrum shows a signal at 175.74 ppm which corresponds to C_3 and C_4 positions of the heterocycle and a signal at 112.08 ppm, which corresponds to the carbons linked to the iron atom of the heterocycle, as selected data.

In the HMQC spectrum an interaction between the signals at 175.74 and 6.34 ppm and another interaction in HMBC between the signal at 112.08 ppm with the signal at 6.34 ppm assigned to the vinylic hydrogens are observed. With these data we find the structure **3b**.

Finally, for the reaction of complex **1** with 1-phenyl-1-hexyn-3-one only one product was formed. Once again, and in the same way as before, there are three possible isomers to form in this reaction.

The 1H -NMR spectrum shows the following signals: 7.46–7.16 ppm a multiple signal which integrates for ten hydrogens; 2.44–2.05 ppm a multiple signal which integrates for four hydrogens corresponding to the two α -methylene groups to the organic carbonyls of the aliphatic substituents; 1.34–1.15 ppm a multiple signal assigned to the four hydrogens of the other two methylene groups and at 0.74 and 0.48 two triplet signals assigned to the two methyl groups of the molecule.

The ^{13}C -NMR spectrum shows a signal at 202.12 ppm assigned to the organic carbonyls; 175.47 and 170.96 ppm the signals for the C_4 and C_3 positions, respectively and two signals at 146.54 and 132.90 ppm assigned to C_2 and C_5 , as selected data. The mentioned data are in agreement with the proposed structure **4**.

In all reactions organic substances containing nitrogen were not detected. This means that the reactions must take place only by thermal decomposition of the complex **1** to produce $Fe(CO)_3$ to initiate the coupling reactions.

3. Experimental

3.1. Material and apparatus

All operations were performed in nitrogen or argon atmosphere with rigorous exclusion of oxygen and moisture using Schlenk or vacuum-line techniques. Solvents

used were dried previously and freshly distilled under argon: benzene from sodium; ethyl ether from sodium and benzophenone. Phenylacetylene and diphenylacetylene were obtained from commercial sources and used as received. 1-Phenyl-1-hexyn-3-one was prepared as reported by Bradsma [5].

The IR spectra were determined in a Nicolet FT-IR Magna 750 apparatus in solution with $CHCl_3$ or KBr bar techniques.

The 1H and ^{13}C -NMR spectra were obtained from a JEOL-GX300 spectrophotometer (300 MHz for 1H and 75 MHz for ^{13}C), using $CDCl_3$ as solvent and TMS as internal reference.

The mass spectra were recorded in a JEOL JMS-Ax505HA, using the FAB^+ and EI techniques.

Melting points were determined in a Melt-Temp apparatus and are not corrected. The reaction yields were determined by dry weight of the purified samples.

3.2. Synthesis of complex **2**

In a flask was placed complex **1** (1.0 g, 2.73 mmol), diphenylacetylene (0.5 g, 3.27 mmol) and benzene (50 ml). The mixture was stirred at reflux temperature for 8 h, under nitrogen atmosphere. During the reaction the conversion was monitored by thin layer chromatography. Then the mixture was cooled and filtered through an Al_2O_3 pad. The filtrate was evaporated to dryness. The residue was purified through silica gel column chromatography using *n*-hexane as eluent. Recrystallization from *n*-hexane–acetonitrile gave 0.240 g (30%) of **2** as orange solid, m.p. 170–174°C (desc.).

3.3. Synthesis of complexes **3a** and **3b**

An analogous procedure was followed as above. The residue obtained after solvent evaporation was purified through silica gel column chromatography using *n*-hexane–ethyl acetate (95:5) as eluent. Then the fraction containing the mixture of complexes **3a** and **3b** was purified by preparative chromatography. Complex **3a** was obtained as yellow solid (345 mg, 22%) and complex **3b** was obtained as oil (315 mg, 17%).

Complex **3a**, $C_{16}H_{12}Fe_2(CO)_6$. MW calc.: 484.0288. MW found: 483.9333. IR ($CHCl_3$, cm^{-1}): 2071, 2036, 1999 (M–CO). MS- FAB^+ (m/z): 484 (M^+), 456 ($M^+ - CO$), 428 ($M^+ - 2CO$), 400 ($M^+ - 3CO$), 372 ($M^+ - 4CO$), 344 ($M^+ - 5CO$), 316 ($M^+ - 6CO$).

Complex **3b**, $C_{16}H_{12}Fe_2(CO)_6$. MW calc.: 484.0288. MW found: 483.9333. IR ($CHCl_3$, cm^{-1}): 2069, 2038, 2000, 1944 (M–CO).

3.4. Synthesis of complex **4**

An analogous procedure was followed as above. The residue obtained after solvent evaporation was purified

through silica gel column chromatography using *n*-hexane–ethyl acetate (97:3) as eluent. Complex **5** was obtained as yellow oil (675 mg, 25%).

Complex **4**, C₂₄H₂₄O₂Fe₂(CO)₆. MW calc.: 624.2113. MW found: 624.0240. IR (CHCl₃, cm⁻¹): 2078, 2047, 2010 (M–CO). MS-FAB⁺ (*m/z*): 624 (M⁺), 596 (M⁺ – CO), 568 (M⁺ – 2CO), 540 (M⁺ – 3CO), 512 (M⁺ – 4CO), 484 (M⁺ – 5CO), 456 (M⁺ – 6CO).

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